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(54) HIGH-SOLIDS TIO2 PIGMENT AND METHOD FOR MAKING SAME

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Titanium dioxide pigment for use in coating compositions, rubber, paper and the like has for years been produced by the so-called sulfate process or the chloride process, as the case may be, and in either case the finished pigment is in the form of a finely divided dry powder which is bagged for shipment. Usually large scale commercial operations will require a large inventory of various grades of bagged pigment which necessitates huge storage sheds and handling equipment for stacking the bags and carrying the stacked bags from storage to transportation facilities such as trucks or railroad cars. This multiple handling of the bagged pigment inevitably results in losses from broken bags. Moreover a similar situation exists at the customer end, i.e. bag breakage with loss of pigment. Further, it is well recognized that the effectiveness of a pigment in coating compositions, as an additive in paper manufacture and the like depends in large measure on how well the pigment disperses in the particular medium to which it is added. When the pigment is shipped in bags the customer must not only empty the individual bags by hand but also must add one or more dispersing agents to his particular formulation. The dispersion of finely divided solids and in particular titanium dioxide pigment in liquid media involves phenomena which are only partially understood even by research chemists and consequently for most customers the problem of effecting optimum dispersion of the pigmentary TiO_2 in a given liquid is largely one of trial and error.

The pumpable high-solids TiO_2 pigment slurry of this invention comprises anatase or rutile TiO_2 pigment uniformly dispersed in a medium which may be water, a solvent or combination of water and solvent plus organic reagents selected to impart desirable properties to the slurry such as suspension, freedom from foaming, resistance to biological degradation and suitable viscosity for handling purposes.

The TiO_2 pigment may be a dry, finished pigment prepared

by the sulfate or the chloride process, as the case may be, and treated with various metal oxides such as Al_2O_3, TiO_2, ZrO, and SiO_2; or may be a dry or wet pigment-intermediate i.e. treated or untreated calciner discharge. The percentage of TiO_2 pigment contained in the slurry is, in keeping with the objects of this invention, relatively high, 50% and preferably 60% being the lower limit and from 75-80% being the upper limit, the latter being dependent upon such factors as the water and/or oil demand of the TiO_2 pigment used, and the degree of dilatancy that can be tolerated at acceptable pumping rates. For the expected uses of the TiO_2 pigment slurry of this invention the TiO_2 pigment slurries would generally be shipped at from 60-80% solids on a TiO_2 weight basis. The slurry is prepared by adding the TiO_2 pigment with vigorous agitation to an aqueous or solvent medium or mixtures thereof, containing a combination of one or more dispersing agents, a thickening agent and optionally a defoamer and a mildewcide. The dispersing agents are di-polar compounds of high molecular weight, typical dispersants being the polyphosphates such as potassium tripolyphosphate and sodium hexametaphosphate; and amines such as triethanolamine or monoisopropanolamine. The thickening agent serves to inhibit settling and add the desired viscosity characteristics to the slurry and may be a cellulose derivative such as methyl-hydroxyethyl or sodium carboxymethyl cellulose; a polysaccharide gum or the like. Suitable anti-foaming agents may be added to inhibit excessive foaming during mixing. These would include silicones, petroleum solvents and phosphates, typical phosphates being iso octyl phosphate, triethyl phosphate, tri octyl phosphate or tri-N-butyl phosphate. The mildewcides may be added to prevent undesirable bacterial growth during extended storage and may include phenols such as pentachlorophenol, 2,4,5-trichlorophenol 2, 3,4,6 tetrachlorophenol or the like; or mercurials such as ~~phenol~~ phenyl mercury oleate, phenyl mercury acetate and the like.

The above mentioned reagents are illustrative only of the kinds of dispersing agents, thickening agents, defoamers and mildewcides that have been used successfully in producing the high-solids of this invention but it will be understood that the invention is not limited to these particular reagents but is comprehensive of others as enumerated in the preferred embodiment of the invention which follows.

The TiO_2 pigments used in the slurries of this invention are especially designed to be used in paper and emulsion paints and to this end are rutile pigments having a post calcination treatment with the hydrous oxides of titanium, silicon and aluminum.

To prepare the slurries the aforesaid reagents are added to a medium such as water and thoroughly mixed after which the TiO_2 pigment is added accompanied by vigorous agitation as for example by use of a high speed impeller mill.

The dispersants are used to insure good dispersion of the TiO_2 pigment and as pointed out above are selected from a group of di-polar compounds having a high molecular weight, typical dispersants useful in preparing the high-solids slurries of this invention being polyphosphates such as potassium tripolyphosphate, tetrapotassium pyrophosphate and sodium hexametaphosphate. Other dispersants include the amines such as triethanolamine (TEA) and monoisopropanol-amine (MIPA), sodium salt of carboxylated polyelectrolyte, sodium citrate, sodium gluconate, ethylene oxide condensate (sodium or potassium salt), amino tris methyl phosphonic acid, methyl phosphonate, the sodium salt of condensed mono-naphthalene sulfonic acid, and the like.

The amount of dispersing agent or agents used in preparing the high-solids slurry of this invention is dependent on the amount and type of TiO_2 pigment used as well as the nature of the dispersant itself i.e. whether it is a high or low active disper-

sant. It follows therefore that the dispersant level may vary considerably. In general the amount of dispersant used may vary from about 0.1% to as high as 5.0%, the higher percentages being used with low active dispersants. For all practical purposes however the amount of dispersant used will range from about 0.2% to 2.0% on a TiO_2 basis.

The thickening agent is added to the slurry to reduce pigment settling and to maintain the desired viscosity characteristics essential to good rheology and pumpability. Suitable thickeners include water soluble hydroxy-groups containing organic colloids i.e. cellulose derivatives such as methyl hydroxethyl or sodium carboxymethyl cellulose, starches, polyvinyl alcohols or possibly alginates. Other thickeners that may be used include the "clay" types such as hydrous magnesium silicate or purified magnesium aluminum silicate; and also polysaccharide gum, sometimes referred to as xanthan gum, and certain acrylic type thickeners such as sodium polyacrylate, cross-linking acrylic copolymers and polyacrylic acid solutions.

These thickening agents are used in amounts which depend upon the extent to which they are to influence settling and viscosity. In practice these amounts may vary from 0.0% to as high as 5% but for most applications the amounts used would range from 0.005% to 0.5% on a TiO_2 weight basis.

To form an aqueous high solids slurry of uniformly dispersed TiO_2 pigment it is important that the mixture be stirred vigorously. This frequently causes an excessive build-up of foam or air bubbles which is undesirable in a plant scale operation and hence defoaming or anti-foaming agents are sometimes added to minimize foaming. These agents may comprise the silicones, petroleum solvents and phosphate types such as iso octyl phosphate, tri ethyl phosphate, tri octyl phosphate and the like. Concentrations of these ingredients varywith their strength and type. Normally

these anti-foaming reagents would be used in amounts ranging from 0.005% to 0.5% on a TiO_2 weight basis but amounts as low as 0.001% and as high as 1.0% may be used.

The mildewcide is added to prevent biological degradation of the thickening agents and to inhibit bacterial growth and subsequent putrefaction of the aqueous slurries - especially when the slurry is to be stored over long periods of time. Suitable mildewcides are the phenol types such as pentachlorphenol, sodium salt, mono hydrate; 0-phenyl-phenol; 2,3,4,6 tetra chlorophenol and mercurials such as phenyl mercury 2-ethylhexylmaleate, phenyl mercury oleate, phenyl mercury acetate, phenyl mercuric propionate and the like. These materials may be added in amount ranging from 0.01% to 0.5% and on a TiO_2 weight basis.

The invention is further illustrated by the following examples:

EXAMPLE 1

A predispersed aqueous rutile TiO_2 pigment slurry at 70% solids by weight was prepared as follows:

To 574.8 grams water were added in the order named 0.4 grams of a purified magnesium aluminum silicate as thickener, 14.4 grams potassium tripolyphosphate as dispersant, 6.4 grams of sodium salt of carboxylated polyelectrolyte which also served as a dispersant, 2.0 grams of a silicone type defoamer and 2.0 grams of di(phenylmercury) dodecenyl succinate (10% Hg) which served as a mildewcide. The reagents and water were thoroughly mixed after which 1400.00 grams rutile latex grade TiO_2 pigment were added and dispersed in the aqueous mixture by using a high speed impeller mill to form a homogeneous TiO_2 pigment slurry of 70% solids by weight. Foaming was minimal during mixing and the slurry remained in a uniformly dispersed pumpable condition after storage for a period of 140 days.

EXAMPLE II

A relatively low solids (64%) aqueous TiO_2 slurry was prepared as follows:

To 711,3 grams of water were added in the order named 8.6 grams sodium gluconate as dispersant, 0.1% xanthan gum as thickener and 1280 grams of a rutile latex grade TiO_2 pigment. The ingredients of the slurry were admixed as described in Example I and the final slurry was homogeneous and retained its uniformity and pumpability after 30 days storage.

EXAMPLE III

As a further illustration of the invention a relatively high solids (77%) TiO_2 slurry was prepared using an organic solvent as the liquid medium.

To 376,8 grams propylene glycol were added in the order named 11,2 grams of a silicone which served as a defoamer, 62,0 grams sodium salt of carboxylated polyelectrolyte as dispersant and 1550,0 grams rutile TiO_2 pigment.

The ingredients were mixed as described in Example I and the final slurry was homogeneous and had suitable viscosity for handling purposes even after 60 days of storage.

EXAMPLE IV

The scope of the invention is further illustrated by an example in which the liquid medium was a mixture of water and an organic solvent. Thus to 308,2 grams water and 92,4 grams ethylene glycol was added 9.2 grams potassium tripolyphosphate and 24,6 grams alkylphenoxypoly (oxyethylene) ethanol as dispersing agents, 18,4 grams tri-octyl phosphate as defoamer and 6,2 grams di(phenylmercury) dodecenyl succinate (10% Hg) as a mildewcide. To the above was added and dispersed, 1541,0 grams of titanium pigment.

This slurry also had acceptable rheology after 30 days of storage.

While this invention has been described and illustrated by

the examples shown, it is not intended to be strictly limited hereto, and other variations and modifications may be employed within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

1. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment, said slurry comprising: a liquid medium selected from the group consisting of water, an organic solvent and mixtures thereof, from 60 to 80% TiO_2 pigment, an organic dispersing agent in an amount in the range of from 0.1% to 5.0% and an organic thickening agent in an amount from 0.0% to 5.0%

2. As a new product of manufacture a pumpable high solids slurry of uniformly dispersed TiO_2 pigment according to Claim 1 wherein said slurry includes an organic defoamer in an amount from 0.005 to 0.5%.

3. As a new product of manufacture a pumpable high solids slurry of uniformly dispersed TiO_2 pigment according to Claim 1 wherein said slurry includes a mildewcide in an amount from 0.01 to 0.5%.

4. As a new product of manufacture a pumpable high solids slurry of uniformly dispersed TiO_2 pigment according to Claim 1 wherein said slurry includes an organic defoamer and a mildewcide, said organic defoamer being present in an amount from 0.005 to 0.5% and said mildewcide present in an amount from 0.01 to 0.5%.

5. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment according to Claim 1 wherein the liquid medium is water.

6. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment according to any of claims 1, 2 or 3 wherein the liquid medium is a glycol selected from the group consisting of propylene and ethylene.

7. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment according to

any of claims 1, 2 or 3 wherein said dispersing agent is selected from the group consisting of potassium tripolyphosphate, sodium gluconate, sodium salt of carboxylated polyelectrolyte and alkyl-phenoxypoly (oxyethylene) ethanol.

8. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment according to any of claims 1, 2 or 3 wherein said thickening agent is selected from the group consisting of magnesium aluminum sulfate and xanthan gum.

9. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment according to any of claims 1, 2 or 3 wherein said defoamer is selected from the group consisting of silicone and tri octyl phosphate.

10. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment according to claim 5 wherein said dispersing agent comprises sodium gluconate and said thickening agent is xanthan gum.

11. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment said slurry comprising a homogeneous mixture of; 376.8 grams propylene glycol, 1550 grams TiO_2, 11.2 grams silicone as defoamer and 62.0 grams sodium salt of carboxylated polyelectrolyte as dispersant.

12. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment said slurry comprising: an aqueous homogeneous mixture of 711.3 grams water, 8.6 grams sodium gluconate as dispersant, 0.1 grams xanthan gum as thickener and 1280 grams of TiO_2 pigment.

13. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment said slurry comprising; an aqueous homogeneous mixture of 574.8 grams of H_2O, 1440 grams TiO_2 pigment, organic dispersing agents consisting of 14.4 grams potassium tripolyphosphate and 6.4 grams sodium salt of carboxylated polyelectrolyte, an organic thickening agent consisting of 0.4 grams magnesium aluminum silicate, 2.0

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grams silicone as defoamer and 2.0 grams di(phenylmercury) dodecenyl succinate (10% Hg) as mildewcide.

14. As a new product of manufacture a pumpable high-solids slurry of uniformly dispersed TiO_2 pigment said slurry comprising: an aqueous homogeneous mixture of 308.2 grams water, 92.4 grams ethylene glycol, organic dispersing agents consisting of 9.2 grams potassium tripolyphosphate and 24.4 grams alkylphenoxypoly (oxethylene) ethanol, a defoamer consisting of 18.4 grams tri octyl phosphate and moldewcide consisting of 6.2 grams di(phenylmercury) dodecenyl succinate (10% Hg) and 1541.0 grams TiO_2 pigment.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente